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Magnetic and magnetocaloric properties of Ho_6Co_2Ga-type $Dy_6Co_{2.5}Sn_{0.5}$ compound

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ABSTRACT

DC magnetization studies on $Dy_6Co_{2.5}Sn_{0.5}$ compound (orthorhombic, Ho_6Co_2Ga-type, space group *Immm*, No. 71) have been carried out in the temperature range of 2–300 K and in magnetic fields up to 140 kOe. A field induced metamagnetic transition is observed below its Néel point of 42 K (at 2 K the critical field H_c is 37 kOe). Magnetization-field isotherms have been measured for this compound near magnetic transition temperatures from which isothermal magnetic entropy change, ΔS_m, has been computed. The maximum ΔS_m values of –5.2 J/kg K (for a field change of 80 kOe) and +6.5 J/kg K (for a field change of 50 kOe) are observed at 52 K and 13 K, respectively.

1. Introduction

The compound $Dy_6Co_{2.5}Sn_{0.5}$ belongs to the series of ternary $R_6\{Co, Ni\}_{3-x}\{Ga, In, Sn, Pb, Bi\}_x$ compounds [1–13], which crystallize in the orthorhombic Ho_6Co_2Ga-type structure (space group *Immm*, No. 71) [13]. Interest in this series of compounds arises because of its structure that is an orthorhombic derivative of the cubic $Sm_{12}Ni_6In$-type structure [14]. Thus, these compounds may demonstrate the magnetostructural transition of rare earth sublattice ordering similar to that observed in well-known series of $Gd_5Si_{4-x}Ge_x$ (x=0–4) compounds (see for e.g. [15]). The compounds $Tb_6Co_{2.35}Sn_{0.65}$ [8] and $\{Gd–Tm\}_6Co_{2.5}Bi_{0.5}$ [10] exhibit antiferromagnetic ordering with field induced metamagnetic transition in the ordered state, whereas magnetic structure of Er_6Ni_2Sn is complex non-collinear commensurate antiferromagnet with strongly reduced Er magnetic moments [11].

The present work reports magnetic properties and magnetocaloric effect of $Dy_6Co_{2.5}Sn_{0.5}$ as representative of a series of Ho_6Co_2Ga-type rare earth compounds.

2. Experimental details

The $Dy_6Co_{2.5}Sn_{0.5}$ sample was prepared by arc-melting the weighed amounts of Dy (purity 99.9 wt%), Co (99.95 wt%) and Sn (99.99 wt%). The sample was annealed at 970 K for 200 h in an argon atmosphere and subsequently quenched in ice-cold water. The sample quality was evaluated using powder X-ray diffraction and X-ray spectral microprobe analyses. The X-ray data were obtained on a DRON-3.0 diffractometer (Cu K_α radiation, 2θ=20–90°, step 0.05°, 2 s per step). A "Camebax" microanalyser was employed to perform X-ray spectral analyses of the samples (15 kV, 3×10^{-8} A, *K*-, *L*- and *M*-lines, 2×2 μ^2).

The unit cell data were derived using the Rietan-program [16] in the isotropic approximation.

Magnetization measurements on polycrystalline samples were carried out using a vibrating sample magnetometer (VSM attachment on PPMS Dynacool System, Quantum Design, USA) in the temperature range of 2–300 K and in magnetic fields up to 140 kOe. Low field (100 Oe) magnetization data were obtained in zero-field-cooled (zfc) and field-cooled (fc) states to determine the magnetic ordering temperatures. Magnetization as a function of temperature was measured in 5 kOe field in zero-field-cooled state to obtain effective paramagnetic moment and paramagnetic Curie temperature. Magnetization-field hysteresis curve was recorded at 2 K to obtain saturation magnetization and coercive field. Magnetization-field isotherms were obtained at various temperatures ranging from 2 K to 102 K with a temperature step of 5 K and a field step of 2.5 kOe to calculate isothermal magnetic entropy changes.

The paramagnetic susceptibility was fitted to Curie–Weiss law and the effective magnetic moment and paramagnetic Curie temperature were obtained [17]. Magnetocaloric effect (MCE) is calculated in terms of the isothermal magnetic entropy change, ΔS_m, using the magnetization vs. field data obtained near the

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Table 1
Unit cell data of orthorhombic derivative of $Sm_{12}Ni_6In$-type structure [14] [a]: Ho_6Co_2Ga-type $Dy_6Co_{2.5}Sn_{0.5}$ [a=0.93718(6) nm, b=0.93910(6) nm, c=0.98754(6) nm] (space group *Immm* No 71, *oI*36), Z=4, atomic displacement parameters of all atoms β_{11}=0.002846, β_{22}=0.002835, β_{33}=0.002563 ($\beta_{11}=B_{11}/[2a]^2$, $\beta_{22}=B_{22}/[2b]^2$, $\beta_{33}=B_{33}/[2c]^2$), R_F =3.3%.

(a) Atomic positions

Atom	Site	*x*/*a*	*y*/*b*	*z*/*c*	Occupancy
Dy1	8n	0.2872(8)	0.1881(8)	0	1.00
Dy2	8m	0.2977(9)	0	0.3147(6)	1.00
Dy3	8l	0	0.1956(8)	0.2170(7)	1.00
Co1	4j	1/2	0	0.1145(20)	1.00
Co2	4g	0	0.3745(23)	0	1.00
Co3	2a	0	0	0	1.00
Sn	2b	0	1/2	1/2	1.00

(b) Interatomic distance (ESD ± 0.0005 nm) and their ratio to sum of the atomic radii of corresponding atoms [20] $\Delta=D/(R_{atom1}+R_{atom2})$, ($\Delta \le 1.12$) and coordination number δ.

Atom-Atom	*D* (nm)	Δ	Atom-Atom	*D* (nm)	Δ	Atom-Atom	*D* (nm)	Δ
Dy1- 2Co1	0.28884	0.96	Dy2- 1Co1	0.27392	0.91	Dy3- 1Co2	0.27464	0.91
1Co3	0.32143	1.06	2Co2	0.28714	0.95	1Co3	0.28225	0.93
1Co2	0.32366	1.07	1Sn	0.33366	1.05	1Co1	0.33077	1.09
2Dy3	0.34414	0.97	2Dy3	0.34444	0.97	1Sn	0.33444	1.05
1Dy1	0.35141	0.99	2Dy3	0.34769	0.98	2Dy1	0.34414	0.97
1Sn	0.35513	1.12	2Dy1	0.35519	1.00	2Dy2	0.34444	0.97
2Dy2	0.35519	1.00	2Dy1	0.35715	1.01	2Dy2	0.34769	0.98
2Dy2	0.35715	1.01	1Dy2	0.36598	1.03	2Dy1	0.36057	1.02
2Dy3	0.36057	1.02	1Dy2	0.37918	1.07	1Dy3	0.36738	1.04
	δ=14			**δ=14**			**δ=13**	
Co1- 1Co1	0.22615	0.90	Co2- 1Co2	0.22820	0.91	Co3- 4Dy3	0.28225	0.93
2Dy2	0.27392	0.91	2Dy3	0.27464	0.91	4Dy1	0.32143	1.01
4Dy1	0.28884	0.96	4Dy2	0.28714	0.95		**δ=8**	
2Dy3	0.33077	1.09	2Dy1	0.32366	1.07			
	δ=9			**δ=9**		Sn- 4Dy3	0.33444	1.05
						2Dy2	0.33366	1.05
						4Dy1	0.35513	1.12
							δ=12	

[a] The $Sm_{12}Ni_6In$-type structure in term of *Im*-3 and *Immm* space groups: *Im*-3 space group, $a_{Sm12Ni6In}$, Sm 24g (0, y_{Sm}, z_{Sm}); Ni 12e (1/2, 0, z_{Ni}), In 2a (0, 0, 0); *Immm* space group: $a=b=c=a_{Sm12Ni6In}$, Sm1 8n (y_{Sm}, z_{Sm}, 0), Sm2 8m (z_{Sm}, 0, y_{Sm}), Sm3 8l (0, y_{Sm}, z_{Sm}), Ni1 4j (1/2, 0, z_{Ni}), Ni2 4h (0, z_{Ni}, 1/2), Ni3 4f (z_{Ni}, 1/2, 0), In 2a (0, 0, 0).

magnetic transition using the thermodynamic Maxwell equation [18].

3. Results and discussion

From X-ray spectral and X-ray powder analysis, the '$Dy_6Co_{2.5}Sn_{0.5}$' sample contains 0.98(1) mass fraction of Ho_6Co_2Ga-type $Dy_6Co_{2.5}Sn_{0.5}$ ($Dy_{67(1)}Co_{27(1)}Sn_{6(1)}$ phase) and 0.02 (1) mass fraction of $MgCu_2$-type $DyCo_2$ [19] (a=0.7188(5) nm, R_F=3.5%, $Dy_{34(1)}Co_{66(1)}$ phase). The atomic position parameters and interatomic distances (in comparison with atomic radii of Dy, Co and Sn [20]) of $Dy_6Co_{2.5}Sn_{0.5}$ are listed in Table 1.

Low field zfc and fc magnetization data of $Dy_6Co_{2.5}Sn_{0.5}$ obtained in applied fields of 100 Oe and 5 kOe indicate a slope change at 152 K and also a low-temperature antiferromagnetic transition at 42 K (Fig. 1a and b).

The paramagnetic susceptibility of $Dy_6Co_{2.5}Sn_{0.5}$ in an applied field of 5 kOe follows the Curie–Weiss law in the temperature range of ~180–300 K (inset in Fig. 1b). The fit to the Curie–Weiss law yields a positive paramagnetic Weiss temperature Θ_p=27.9 K and an effective magnetic moment per formula unit (M_{eff}/fu) of 26.11(7) μ_B. This M_{eff}/fu yields an effective magnetic moment per Dy^{3+} of 10.66(2) μ_B in $Dy_6Co_{2.5}Sn_{0.5}$, which almost coincides with the theoretical Dy^{3+} moment of 10.645 μ_B [21] and Co probably carries no appreciable magnetic moment in $Dy_6Co_{2.5}Sn_{0.5}$. The positive paramagnetic Weiss temperature indicates the presence of ferromagnetic interactions in $Dy_6Co_{2.5}Sn_{0.5}$.

The ferrimagnetic ordering temperature of $DyCo_2$ is around 140 K [22] and this secondary phase is present only up to 0.02

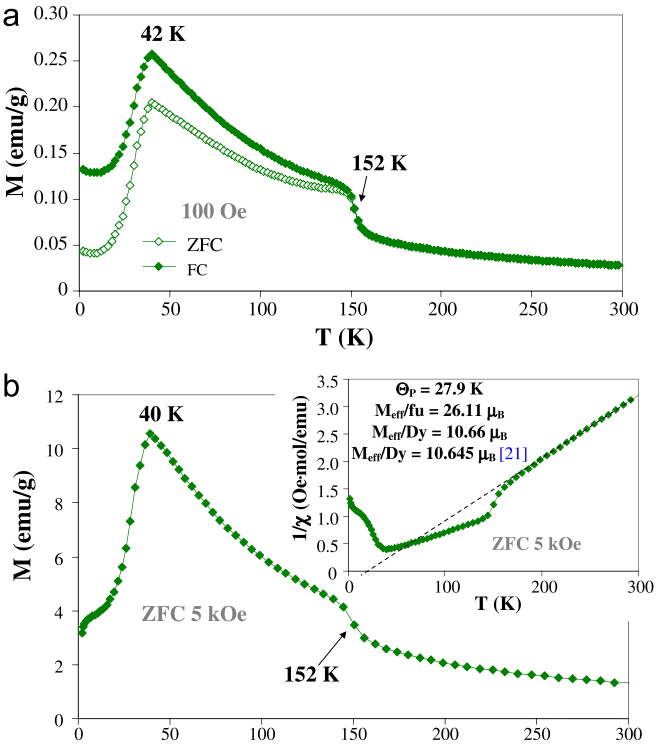

Fig. 1. Magnetization of $Dy_6Co_{2.5}Sn_{0.5}$ as a function of temperature (a) in applied field of 100 Oe and (b) magnetization and inverse magnetic susceptibility vs. T of $Dy_6Co_{2.5}Sn_{0.5}$ in applied field of 5 kOe.